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Flexible All-Gel-Based Supercapacitors

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Flexible All-Gel-Based Supercapacitors

By

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Abstract

Flexible All-Gel-Based Supercapacitors

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Abstract: Flexible energy storage devices are important sources of power for flexible electronics such as role up screens and wearable electronics. Most of the flexible energy storage devices are based on using either carbon nanomaterials or using composite electrodes (carbon nanomaterials with conductive polymers). The main drawbacks of these approaches are: the cost, fabrication time consuming and difficulty of synthesizing proper carbon nanomaterials. An alternative promising approach is using the 3D nanostructured conductive polymer hydrogel, which exhibits good electrochemical performance and good mechanical properties. 3D nanostructured hydrogel has a porous nanostructured network, which has many advantages such as providing short pathways for electron transport and increasing the electrode-electrolyte penetration depth via pores. In addition, the porous structure can contribute to release chain's strains due to the volume change during the charge-discharge processes. For energy storage devices that work under periodically critical engineering stresses, these hydrogels may suffer from micro cracks, which lead to degraded electrochemical performance over time, so increasing the flexibility of 3D nanostructured hydrogel is very important for flexible energy storage devices. In this thesis,

we propose a new idea of synthesizing hybrid gel electrodes that are composed of 3D nanostructured hydrogel and small percentages of nonconductive gel (PANI+PEO). The conductive hydrogel was contributed to provide good electrochemical performance, and the nonconductive gel was used as a plasticizer to increase the flexibility of the hybrid gel electrodes. Adding small percentage of the plasticizer polymer in a controllable manner has kept high electrochemical performance, and greatly enhanced the mechanical properties of the flexible gel electrodes. In order to approve our idea, we designed three gel supercapacitors based on the differences in the PEO content in the hybrid gel electrodes, and then we performed a wide comparison among them in terms of electrochemical performance and the mechanical behavior.

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Chapter 1: *Introduction*

Conductive polymers (CPs) are a class of materials that have a good electrical conductivity and owning other properties common of conventional polymers such as flexible in processing and simple in synthesizing.[1] Conductive polymers have a good electrical conductivity, and this conductivity comes from π-conjugated chains and doping process with special dopants and proton donors, which provide fast reversible Faradic reactions.[2] The conductivity of CPs is controlled by the doping level and molecular structure; thus, they could exhibit a wide range of compatibility with different applications such as flexible energy storage devices, biosensors, and medical applications such as medical electrodes.[2, 3] Till now, the most widely used conductive polymers are polyaniline (PANI)[4], polypyrrole (PPY)[5], and polythiophene (PTs)[6]. The advance in understanding the Nanotechnology has opened ways to prepare more reliable conductive polymer gels. These gels have higher electrical and mechanical properties than bulk conductive polymers due to its micro porous structure which provides high surface area and easy and short pathways for electrons and ions to transport.[2] Conductive polymer gels could be prepared by two ways: the first one is by processing the polymerization process of the conductive monomers in the presence of a nonconductive polymer gel matrix (conventional method).[2] The second way is by polymerizing the conductive monomer with the nonconductive monomer together. In the conventional method, nonconductive gel matrix was used as a frame for the conductive gel construction. The conductive monomer is pulled out during the reswollen process of the hydrogel frame.[2] Then, the polymerization process of the conductive monomer occurs by adding chemical oxidants. PPy-pHEMA poly (2-

hydroxyethyl methacrylate)[2, 7] has been produced by this method. The second way is by polymerizing the conductive and nonconductive monomers together, so the nonconductive polymer works as a cross-linker to link the conductive elements.[2] Conductive polymer gels (CPGs) synthesized by the conventional method may have some electrochemical performance degradation during long term of working especially for the electrical conductivity issues. In terms of the scalability, CPGs produced by the conventional method may have limited scalability due to difficulty of controlling the synthesizing processes. [2] Since the conventional preparation method have a noticeable limited scalability, recently, novel synthesizing method has been used to prepare conductive polymer hydrogels CPHs by using special types of dopants and cross linkers. Conductive polymer hydrogels represent a class of materials that evolved from crosslinking polymeric chains in three dimensional scale by using multi-functional group dopants and cross linkers such as phytic acid and phthalocyanine-3,4′,4″,4‴-acid tetra-sodium salt (CuPcTs).[8, 9] Three dimensionally interconnected conductive polymers maintain water inside their porous structure, but they are not soluble in water. CPHs have useful range of pores extended from meso to micro pores inside their structure. The porous structure range of CPHs with the nanofibers interconnected network enables CPHs to exhibit higher flexibility and provides short pathways for electrons to transport, and also enables them to show perfect electrodes-electrolyte penetration, which will facilitate simplifying the ionic transport. In addition, the porous structure contributes to release the polymeric chains strain that resulting from the volume change during the charge-discharge processes. Two well-known nanostructured conductive polymer hydrogels have been prepared by using multi-functional group dopant-

cross linker molecules. The first one is the polyaniline (PANI) hydrogel,[8] and the second is the polypyrrole (PPy) hydrogel.[9] PANI hydrogel has been exhibited unique electrical and mechanical properties which made it useful for many applications such as flexible energy storage devices and biosensors.[2] In energy storage devices, PANI was used either as an electroactive (capacitive) material deposited on flexible substrates, or as a binder for carbon and transition metal oxides which are used for electrodes synthesizing processes in rechargeable batteries. Figure 1 shows PANI hydrogel chemical structure and the pores range.[8]

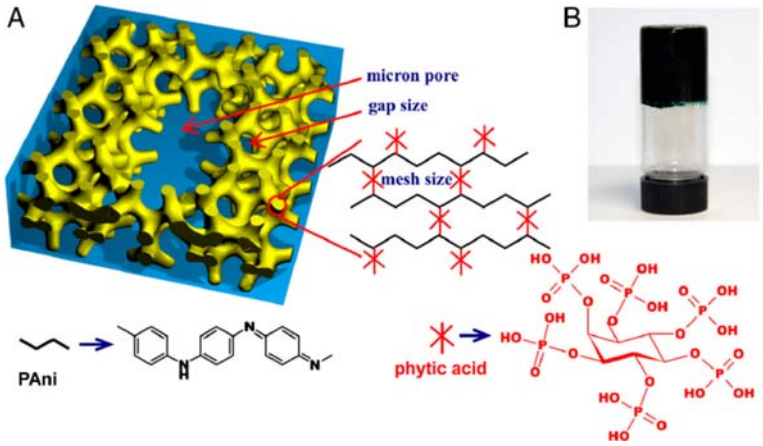

Figure 1. Chemical structure of phytic acid gelated and doped PANI hydrogel. (A) Schematic 3D microstructure of PANI hydrogel. (B) Digital photo shows PANI hydrogel inside transparent glass vial.[8]

In the energy storage applications, PANI hydrogel is very useful due to its unique electrical properties such as high electrical conductivity, high specific capacitance, good rate capability and stable cycling performance.[8] Owning these electrical properties made PANI favorable in synthesizing supercapacitor electrodes. furthermore, PANI was used in

the biosensor applications. Enzymes are soluble in water, so keeping them as stable or immobilized is so important to prevent the sensor signal decay over time. PANI has a good amount of phosphate groups in phytic acid which promotes the enzyme immobilization through the interaction between the phosphate groups in the hydrogel and the imine groups in the enzyme.[8] The chemical interaction that occurs this way will keep the sensor signal without decay. Moreover, the facial of processing PANI hydrogel from solution has been made it useful ink for 3D printers. 3D printing technique is a very useful production method to produce inexpensive highly scalable energy storage devices.

On the other hand, controlled structures of PPy hydrogel were prepared by using CuPcTs as a dopant and a cross linker to link the PPy polymeric chains in one dimensional nanofiber.[9] CuPcTs enhanced the electrical conductivity of the hydrogel by two orders increase than when using other dopants. PPy nanostructured hydrogel has good electrical properties such as high specific capacitance, good cycling performance, good rate capability which make it useful as an electroactive material for batteries and supercapacitor electrodes. Figure 2 shows the chemical structure off CuPcTs doped PPy.

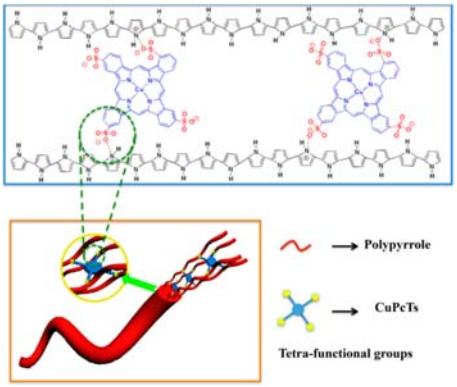

Figure 2. The synthetic process of CuPcTs doped gelated PPy hydrogel.[9]

Chapter 2: *Motivation and Background*

2.1 Flexible Solid State Supercapacitors

There are great demands for increasing power and energy of portable flexible electronics such as roll up screens, bendable solar cells, and wearable electronics. These demands have stimulated great efforts to create and develop flexible, light weight, safe, and environmentally friendly energy storage devices. Flexible solid state supercapacitors are promising energy storage devices to increase the power density for many electric and electronic applications. Electric vehicles and hybrid electric vehicles are some examples of high power systems that powered by supercapacitors.[10-12] Depend on the charge-storage mechanism, supercapacitors are classified into two categories: the first one is the electrical double layer capacitors (EDLCs), and the second is pseudocapacitors.[12] In the first type, the charge storage occurs via electrode-electrolyte interface "(physical contact without redox reversible reactions)". In EDLCs, the surface area and the pores size of the electroactive material determine the value of the specific capacitance;[13] therefore, carbon based materials (CNT, graphene, SWCNTs, and MWCNTs) are preferred active materials for EDLCs.[12, 14] EDLCs provide stable charge-discharge cycling performance and high power density, but the main drawback of EDLCs is that they have low energy density, which is corresponding to the limited capacitance of the active carbon materials. The second type of supercapacitors is the pseudocapacitors. In this type, in addition to physical process of the charge-discharge storage, there are fast redox reversible reactions occurred; therefore, the charge is stored via redox reactions also. Transition metal oxides and conductive polymers are active materials in this type of supercapacitors. By using these

types of active materials, supercapacitors provide high specific capacitance compared to EDLCs. The main drawback of pseudo capacitors is the poor rate capability of transition metals and conductive polymers.[12] In order to synthesize flexible supercapacitors, either flexible EDLCs or flexible pseudocapacitors, two main factors are important to determine the success of the design. The first one is how to design flexible electrodes (cathode and anode). The second one is how to synthesize good ionic conductor and very flexible gel electrolyte. It is important here to review some recent efforts that have been made to develop both flexible electrodes and flexible electrolytes.

2.2. Flexible Electrodes Development

One of the main challenges is to synthesize a flexible electrode that has good mechanical properties without losing some of the electrochemical performance. Many materials have been studied to produce flexible electrodes. Till now carbon based materials, such as carbon nanotubes (CNTs), single wall carbon nanotubes (SWCNTs), multiwall carbon nanotubes (MWCNTs), and graphene are found to be remarkable materials to synthesize flexible energy storage devices due to their good mechanical properties, large surface area, and high electrical conductivity.[12, 15] According to the electroactive materials, flexible electrodes are: carbon based electrodes and composite electrodes. In each type, there are wide range of works and remarkable efforts have been done to develop flexible energy storage devices.

2.2.1. Carbon Based Flexible Electrodes

Researchers have been made great efforts to develop this part of energy storage devices by using variety of carbon materials (0D), (1D), and (2D). Hu and his colleagues have reported the design of flexible supercapacitor based on SWCNTs-water solution printed on both sides of Xerox printing paper by using Meyer rod coating and ink-jet printing technique.[16] The flexible supercapacitor synthesized here exhibited specific capacitance of 33 F/g and specific power of 250, 000 W/kg with the use of an organic electrolyte of 1 M $LiPF_6$ in ethylene carbonate. Using commercial flexible paper as substrate to achieve strong bonding with the active material and using very precise printing technique to control dimensions and to control the amount of the coated active material are advantages of this design. The main problem in this design was the micro porous structure of the printing paper that could cause short circuit between both sides of the paper. The authors treated it by coating a thin film of PVDF on both sides of the substrate paper, so PVDF could serve as a membrane to prevent any electrodes contact and permits electrolyte penetration for both sides.[16] Figure 3 shows the schematic design of flexible symmetric supercapacitor.[16]

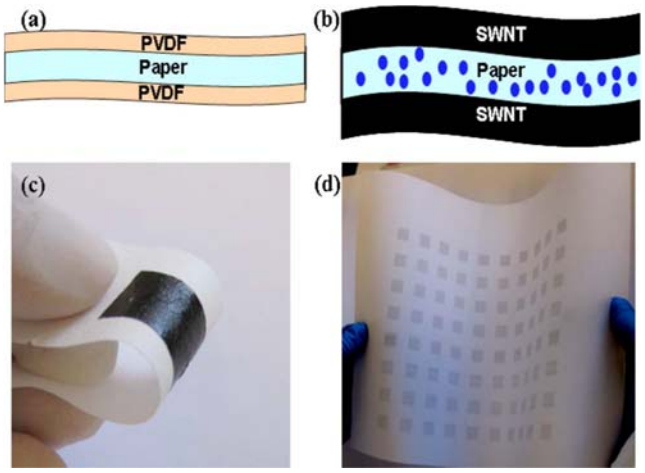

Figure 3. The design of the flexible supercapacitor. (a) Xerox brand printer paper treated by PVDF. (b) Paper supercapacitor structure with SWNT film printed on both sides of the treated Xerox paper. (c) A digital photo of a Meyer rod-coated supercapacitor on printing paper. (d) A digital photo of ink-jet printed supercapacitor on Xerox paper.[16]

In addition, Zheng and his colleagues used solvent-free deposition technique to produce a flexible electric double layer capacitor EDLC. The method was used to attain inexpensive, highly scalable, and light weight device.[17] The method is a drawing on Xerox printing paper by using a pencil.[17] The key point in this design is that the graphite is a conductive material used to draw lithium-air battery electrodes on a ceramic separator.[18] To achieve a uniform strip of a conductive material, they drew electrodes on the Xerox printing paper by using ruler-guided in the same direction of the paper fibers.[17] The resulting strip was very stable at 2 mm bending state as shown in Figure 4 (B). Producing of the supercapacitor was achieved by sandwiching of printing paper between the two conductive strips to prevent any short circuit current as shown in Figure 4 (C).[17]

Figure 4. EDLC prepared by solvent free preparation method. (A) Schematic to draw a conductive strip on a printing paper. (B) Digital photo to show high flexibility of the conductive strip coated on the substrate. (C) Paper flexible supercapacitor design.[17]

The supercapacitor designed by using the solvent free technique is inexpensive and highly scalable, and the electrochemical performance is stable with good areal specific capacitance of 2.3 mF/cm.[17]

3D structured materials like porous cotton textiles[19] and synthetic sponges[20] can be used as a substrate because these materials can provide large surface area and can have good stretchable and compressible features. Hu and his colleagues have synthesized CNTs-cotton electrodes by investigating the dipping-drying process. The areal capacitance was 0.48 F/cm^2, and the specific energy density was 20Wh/kg with high specific power of 10 kW/kg. The electrolyte used in this device was 1 M Na_2SO_4 aqueous solution.[12, 21] Hu and his colleagues have synthesized a new type of a flexible hybrid material based on textile electrode woven by graphene fiber and CNT.[19] Graphene/CNT building block is useful for designing flexible and wearable architectures and devices because it has a combination of large surface area of graphene with very good flexibility and high electrical conductivity of CNTs.[12, 19] Graphene/CNT electrode was synthesized here by intercalating graphene

with Fe_3O_4 nano particles as a catalyst with subsequent CVD growth of CNT.[19] The areal capacitance of flexible supercapacitor designed this way is 0.98 mF/cm^2 at a current density of 20 mA/cm^2, and the specific capacitance tested here is about 200 F/g.[19] Figure 5 shows the schematic illustration of flexible supercapacitor based on graphene/CNT electrodes.

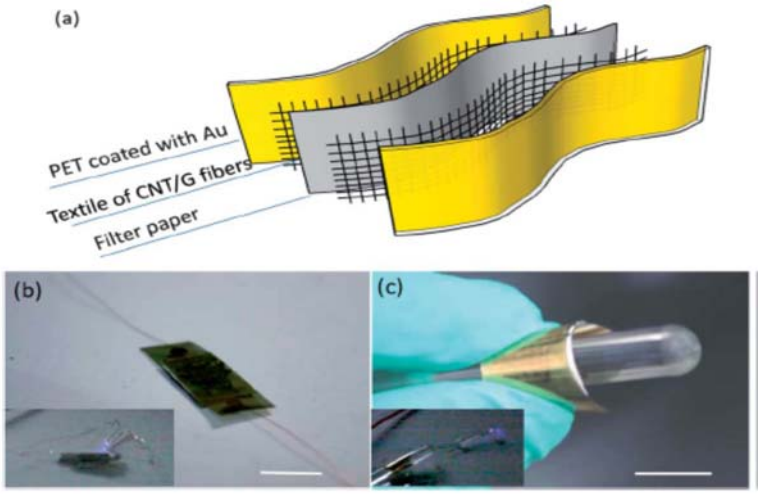

Figure 5. (a) Schematic illustration of a textile of CNT/G fibers as electrodes for supercapacitor. (b and c) Digital photos of the fabricated textile supercapacitor in the flat and bending states, respectively. Insets of (b) and (c) show a light-emitting-diode (LED) lighted by this textile supercapacitor in the flat and bending states. Scale bar: b and c, 1 cm.[19]

2.2.2. Flexible Composite Electrodes

Carbon based materials have good stability and long cycle life with high electrical conductivity; however, the specific capacitance is limited. Conductive polymers and transition metals are pseudo-capacitive materials, so they have higher specific capacitance than carbon nanomaterials. Conductive polymers such as polyaniline (PANI)[22] and polypyrrole (PPY)[23] were widely used as electro active materials for energy storage devices due to their good conductivity and higher specific capacitance. The main drawback of using these two conductive polymers is the poor cycling stability.[12] One of the solutions to overcome this issue is to incorporate conductive polymers with carbon materials which will improve the mechanical properties, electrical conductivity, and cycling stability. Ge and his colleagues have synthesized a flexible and transparent supercapacitor by using SWNT/PANI as electrodes and H_2SO_4 as an electrolyte. The thickness of SWNT is 15 nm coated with PANI by direct electro-polymerization as shown in Figure 6 (A). Figure 6 (B) shows the transparent green color of SWNT/ PANI due to the absorption of the light around 350 and 800 nm by the emerladine salt form of PANI.[24] The supercapacitor designed by using these electrodes (symmetric supercapacitor) and 1 mol/L H_2SO_4 as an electrolyte exhibited 55 F/g at a current density 2.6 A/g and showed the ability to be used as transparent flexible energy storage devices. In addition, this kind of supercapacitor is useful for large scale applications such as bendable screens.[24]

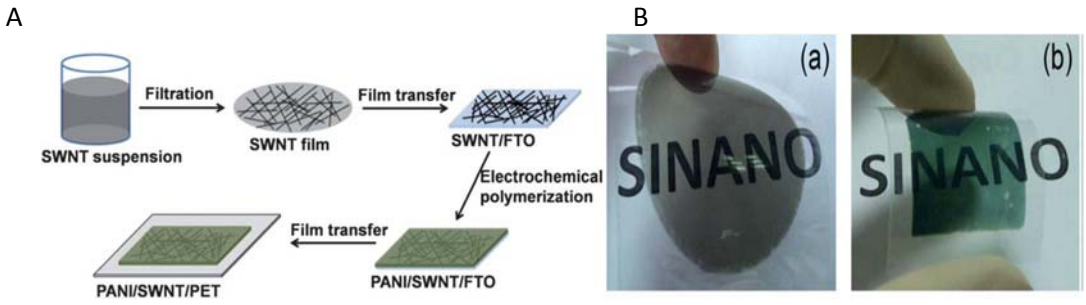

Figure 6. Design of flexible electrodes based on SWNTs/ PANI active materials. A fabrication process of flexible and transparent electrodes. B (a) Is a transparent and a flexible SWNT. (b) Is the transparent and the flexible SWNT/PANI.[24]

On the same hand, Lu and his colleagues have fabricated flexible electrodes for supercapacitor by flow-assembly of the mixture dispersion of graphene (GN) and PPy/CNT. Lu is uniformly distributed a coaxial cable of CNT/PPy between graphene sheets, so that CNT / PPy serves to enlarge the space between graphene layers and provide a pseudo-capacitance to improve the total capacitance of the electrode. Figure 7 illustrates the microstructure and the charge storage mechanism of CNT/PPy/GN composite electrode.[25] The specific capacitance and volumetric capacitance produced by this mechanism are 211 F/g and 122 F/cm^3 at a current density of 0.2 A/g which are higher than the graphene film (73 F/g and 79 F/cm^3).[25]

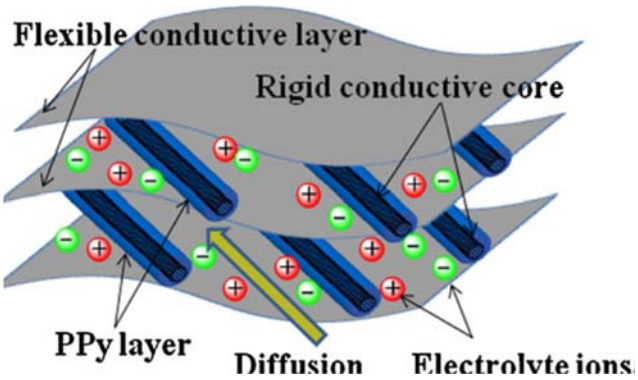

Figure 7. Schematic illustration of the flexible electrode design shows the insertion of CNT/PPy between graphene sheets and illustrates the charge storage mechanism.[25]

The second solution to enhance the cycle life (cycling stability) of the flexible supercapacitors without using the carbon nanomaterials is to use a hierarchically 3D nanostructured polymer gels such as 3D nanostructured PANI hydrogel and PPy hydrogel as active materials deposited on flexible carbon substrates.[26] These gels have microporous structure that could contribute to release the strain caused by the volume change during the charge-discharge. In this approach, Ye and his colleagues have fabricated a very flexible supercapacitor based on PPy hydrogel deposited on a very flexible carbon cloth substrate. The device has been exhibited a very good cycling stability with a very high flexibility and good electrochemical performance.[26]

On the other hand, transition metal oxides such as MnO_2,[27] and NiO[28] exhibit high pseudo capacitive behavior that pushes the energy density of the flexible supercapacitors forward, but the main problem for the transition metal oxide is the poor electrical conductivity. One of the interesting solutions is to hybridize transition metal oxide with carbon based materials as they are well-known of their higher electrical conductivity.

Cheng and his colleagues synthesized a highly flexible and a highly conductive thin film of CNT/G/MnO_2 for flexible supercapacitor electrodes. The resulting device has good mechanical properties such as 48 MPa tensile strength, and it has a high electrical conductivity that comes from CNT and graphene.[29] The specific capacitance of the electrode was 372 F/g which is higher than CNT and graphene. Figure 8 shows the fabrication process of the highly flexible electrode based on CNT/ G/MnO^2**.**

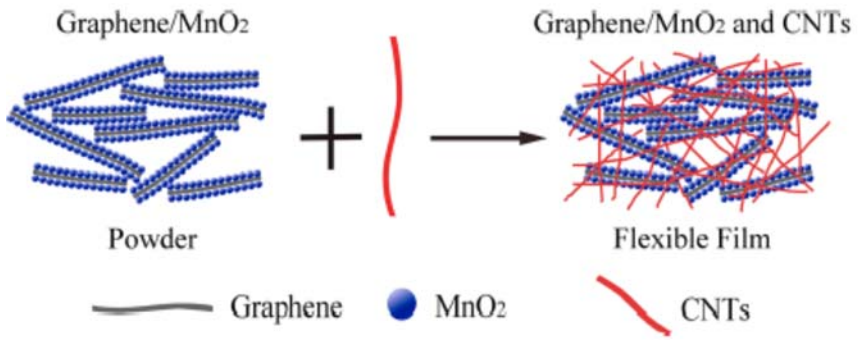

Figure 8. Schematic illustration of the highly flexible and highly conductive film based on CNT/G/MnO2.[29]

2.3. Gel Polymer Electrolyte Development

The second key factor in designing a successful flexible supercapacitor is the solid state electrolyte. Solid state electrolyte could be completely solid or quasi-solid state such as gel polymer electrolyte. Gel polymer electrolyte must have good electrical and mechanical properties such as being easy to handle, having a good ionic conductivity 10^{-3} to 10^{-4} S/cm or better at a wide range of temperatures, non-toxic, stable, wide potential window, and inexpensive.[12] Gel polymer electrolyte is composed of three elements: the first one is the polymer framework as a host such as polyethylene oxide (PEO) and

polyvinyl alcohol (PVA).[30] The second element is an organic/aqueous solvent as a plasticizer, and the third element is a supporting electrolyte salt. Depending on the electrolytic salt, there are three well known categories of gel polymer electrolyte: (1) lithium-gel polymer electrolyte, (2) proton conducting gel electrolyte, and (3) alkaline gel polymer electrolyte.[12] Lithium gel-polymer electrolyte is often prepared by blending dissolved Li salts in an organic solvent with (PMMA, PVA, PAN, etc.) polymers.[12] Many experiments have been conducted to develop polymer gel electrolyte characteristics. Lee and his colleagues have synthesized PMMA/$LiClO_4$ gel electrolyte in order to be used between MnO_2 core-PEDOT shell electrodes for supercapacitor. The method was simply processed by mixing 4.2 mL of 1M lithium perchlorate in a 5: 2 V: V ratio of acetonitrile: propylene carbonate solvent with 0.8 g of PMMA. This mixture was heated with continuous stirring to 105 °C using a hotplate until the solution begins to be gel.[31] The full cell that consists of MnO_2-PEDOT and PMMA/$LiClO_4$ has been exhibited a total capacitance of 0.26 F at a working voltage of 1.7 V, which is useful to provide enough energy to feed small portable and flexible devices. Furthermore, Huang and his colleagues have synthesized a gel polymer electrolyte with high ionic conductivity and wide working potential window. The synthesizing process was done by using polyethylene glycol (PEG) blended with poly acrylonitrile (PAN-b-PEG-b-PAN) as a matrix or host and dimethyl formide (DMF) as a plasticizer with LiClO4 salt.[32] This kind of gel has a very good ionic conductivity of 6.9×10^{-3} S/ cm and has a wide potential window of 2.1 V. Figure 9 shows a photo graph of gel polymer electrolyte film.[32]

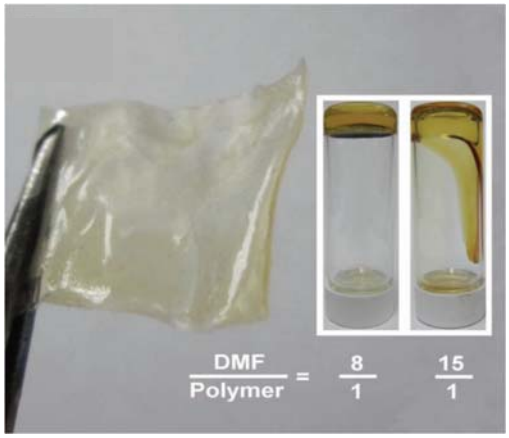

Figure 9. Digital photo of the gel polymer electrolyte. The gel was produced by heating a LiClO4–PAN-b-PEG-b-PAN–DMF mixture at 80°C for half a day, followed by pouring and removing a portion of DMF at 80°C for 1 h. The inset photograph shows the viscosity of the PAN-b-PEG-b- PAN–DMF gel mixtures with changing DMF content.[32]

The second type of gel polymer electrolyte is the proton conducting gel polymer electrolyte. This type of gel electrolyte has simulated many scientific researches due to its unique electrical characteristic.[12] Protons have higher mobility than Li^+ ions which make them very useful to achieve fast charge-discharge processes for supercapacitors.[12] Polymer gel electrolyte is usually prepared by immersing polymer matrix inside a proton donor solution with polar solvent. H_2SO_4 and H_3PO_4 were widely used as proton donors in this type of electrolyte.[12] Recently, researchers have investigated these types of acidic donors with different types of polymer matrices such as PVA/H_2SO_4, and PVA/ H_3PO_4 /silicotungstic acid.[33] Wu and his colleagues have prepared a redox mediate gel electrolyte by mixing P-benzene diol (PB) with PVA/H_2SO_4 gel polymer electrolyte.[30] A gel polymer electrolyte was synthesized here by a solution cast method. Deionized water was used to dissolved 1 g of PVA under agitation at 50°C for four hours and then H_2SO_4 (0.01 mol)

was added to the solution with a constant stirring. PB (0.6 g) was added to the above solution after one hour. Finally, the solution was air-dried at room temperature to produce a gel polymer electrolyte.[30] The advantage of PB is to provide fast and stable redox reaction that can enhance the ionic conductivity and brings pseudo capacitance to the full cell.[30]

The third type of gel polymer electrolytes is alkaline gel polymer electrolyte. This type was widely used in solid alkaline batteries and supercapacitors because it exhibits high ionic conductivity between 20-30 °C, and good anionic transference number.[34] Lewandowski and his colleagues prepared PEO-KOH-H_2O gel polymer electrolyte by the casting technique. PEO was dissolved in DI water and then mixed with KOH solution. The mixture then heated to 60°C for four hours until a homogenous viscous solution was formed. Further air dry process has been done to obtain a reasonable polymer gel electrolyte.[35] PEO-KOH-H2O electrolyte was used as a separator and electrode binders in the fabrication process of the supercapacitor, and it exhibited a good compatibility with active carbon electrodes.[35] Another work has been done by Yang and his colleagues where they synthesized PVA/KOH/H2O gel polymer electrolyte that has a very good ionic conductivity of the order of 10^{-2} S/cm.[36]

In this thesis, we report a new idea of designing highly flexible like bendable, foldable, and twistable gel supercapacitors (carbon free) by using PVA-H_2SO_4 polymer gel electrolyte and blending two hydrogels together to design highly flexible gel electrodes. The first one is a high molecular weight (600,000 g/mol) polyethylene oxide (PEO) which is a nonconductive elastic and soft gel that works as a plasticizer and softener.[37] PEO is used to increase the flexibility and ductility of the gel supercapacitors synthesized here. In terms of ionic conductivity enhancement, PEO gel matrix is available in the electrode material, and since we used gel polymer electrolyte, PEO could increase the interfacial contact between the electrode surface and the gel electrolyte which will simplify and increase the ionic transport, which leads to increasing the ionic conductivity. The second hydrogel is the 3D nanostructured polyaniline hydrogel that has all the electrochemical properties which are required for designing high capacitive gel supercapacitors.[8] In order to control both the mechanical properties and the electrochemical properties of the hybrid gel electrodes, we synthesize different (PEO) weight percentage hybrid gel electrodes. Depending on the mechanical and electrical properties that corresponding to the PEO availability in the hybrid gel electrodes, we design three flexible gel supercapacitors. The first gel supercapacitor is based on PANI-0% PEO, the second is based on PANI-4% PEO, and the third is based on PANI-6% PEO gel electrodes. Electrochemical performance and mechanical behavior are tested to ensure the feasibility of our idea. Many factors indicate that blending two hydrogels to form gel electrodes is advantageous in producing highly flexible gel supercapacitors. These factors include the cost reduction, easiness of synthesizing, and time reduction.

Chapter 3: *Experiments and Characterization Techniques*

3.1. Materials and Chemicals

Carbon cloth (Fuel Cell Earth LLC, MA) has been used as a flexible substrate and as a current collector at the same time. The projected mass load area is 3 cm x 2cm. Poly ethylene oxide (PEO) powder (Sigma-Aldrich) with high molecular weigh 600,000 g/mol was used as a plasticizer. Aniline monomer solution (Ani) is the conductive element which was purchased from (Sigma-Aldrich) and Phytic acid (Sigma-Aldrich) was used as a dopant and a cross linker in the polymerization process. Ammonium persulfate (APS) from (Sigma-Aldrich) was used as initiator and oxidizer. H_2SO_4 acid (98.08 g/mol), and the density is (1.84 g/ml) was used as an aqueous acidic electrolyte and also as a proton donor in the gel-polymer electrolyte. Polyvinyl alcohol (Sigma-Aldrich) was used as a polymer matrix in the synthesizing process of the gel polymer electrolyte.

3.2. Preparation of The Carbon Cloth Substrate

Carbon cloth substrates were used as flexible substrates for gel supercapacitors with the mass load area of (4 cm x 2cm). The substrates have been prepared by immersing them in 6M HNO_3 for 24 hours followed by water purification for 24 hours and ethanol for 12 hours. After that, the drying process at room temperature was done on the substrate followed by UV-Ozone treatment for 15 minutes.[8] Coating the electro-active material directly on the carbon cloth substrate after the ozone treatment to avoid the surface's fast changing from hydrophilic to hydrophobic surface again is important.

3.3. Poly Ethylene Oxide (PEO) Gel Preparation Method

The preparation method has been done by dissolving different masses of PEO powder in deionized water. We prepared different weight percentage samples, but depending on the electrochemical performance and the mechanical behavior of the hybrid gel electrodes we picked up 4% (0.45 mmol) PEO and 6% (0.60 mmol) PEO samples. The preparation method of 4% PEO was done by dissolving 250 mg of high molecular weight (600000 g/mol) PEO in 5 ml of deionized water under heating at 50°C for 12hours. The resulting gel was viscous white colored gel. The same procedure has been performed to prepare 6% PEO with dissolving 350 mg of PEO instead of 250 mg in 5 ml of DI water. Weigh percentage calculation has been done by calculating one ml of PEO solution that contains 50 mg of PEO powder for 4% and 70 mg of PEO for 6% added to the total weight of the conductive polymer solution. We calculated the total weight of the conductive polymer solution, so by this way, we calculated the weigh percentage of PEO with respect to the total weight of the mixed polymeric solutions.

3.4. Polyaniline Hydrogel Preparation Method

PANI was prepared as two solutions mixed together. Solution A consists of 0.286 g (1.25mmol) of APS that was dissolved in 1 ml of DI water under sonication for 10 minutes to ensure the solubility of APS in DI water. Solution B was prepared by mixing 0.458 mL (5 mmol) of aniline with 0.921 ml of Phytic acid and 2 ml of DI water. A and B solutions were put under ice stream at 4°C for 10 minutes to decrease the speed of polymerization process, and then the two solutions were mixed together with fast shacking

for few minutes. After that, the polymer was left for six hours to ensure the completion of the polymerization process. To remove the excessive acid and any unwanted products, the polymer was washed by immersing it in DI water for 24 hours. The dehydrated gel was prepared by heating the polymer in the vacuum furnace for 24 hours.[8]

3.5. PANI-4% and 6% PEO Hydrogels

The synthesizing process was done by preparing solution A and solution B of PANI. Before mixing the two solutions together we added 1 ml (0.45 mmol) 4% of PEO gel to solution B of the PANI with shaking for 5 minutes and sonication for 20 minutes to dissolved the PEO gel inside the solution B to get a homogenous solution. after that, the same steps were done by mixing solution A and B together with fast shaking. Adding PEO to the conductive polymer delays the polymerization time to 15-20 minutes, and made a gradual change in the color of the polymer during the polymerization process from dark brown to yellow and then to dark green. The same procedure was followed to prepare PANI-6% PEO.

3.6. PVA- H_2SO_4 Gel-Polymer Electrolyte Preparation Method

Designing of successful highly flexible gel supercapacitors required three factors: (1) highly flexible substrate, here is the carbon cloth. (2) highly flexible electroactive material to be deposited on the substrate. (3) gel-polymer electrolyte. Here, we prepared PVA-H_2SO_4 gel polymer electrolyte by dissolving 5g of PVA in 40 ml of deionized water with 1M H_2SO_4 under contentious heating at 90°C for 24 hours for agitation. After the agitation, the solution was stirred at the same heat for 3 hours to ensure complete

dissolution of PVA in DI H_2O-H_2SO_4 solution. The resulting gel was white stable very viscous gel.[38] As shown in Figure 10.

Figure 10. Digital photo of the prepared PVA-H_2SO_4 gel-polymer electrolyte

3.7. Design of Symmetric Highly Flexible Gel Supercapacitors

We designed 3-full cells (gel supercapacitors) based on PANI-0% PEO, PANI-4% PEO, and PANI-6% PEO gel electrodes. The substrate was pretreated carbon cloth with mass load's area of (3 cm x 2 cm). The synthesizing process was done by coating the electroactive material (mass load 3 mg) on each substrate with drying them in a vacuum furnace at 60 °C for 12 hours. After that, a thin layer (2-3 mm) of PVA-H_2SO_4 gel electrolyte was coated over the electroactive material in each electrode with leaving them for two hours subjected to an air drying at room temperature to remove the excessive water. then, another thin layer was applied again with the same procedure to prevent any electrodes contact. The final step was done by gently pressing the two electrodes face to face together.

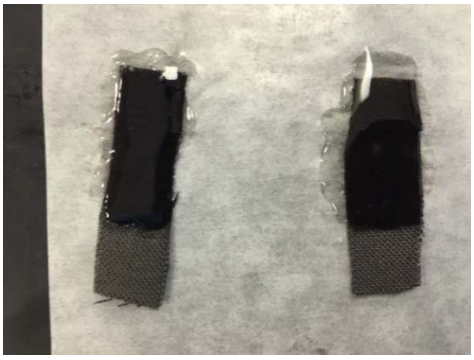

Figure 11. Digital photo shows the coating of gel electrolyte over the polymeric electroactive gel.

3.8. Characterization Techniques

X-Ray diffraction XRD (Rigaku Mini Flex 600) technique was used to characterize the structural changes of the materials after adding PEO to PANI. Fourier transform infrared (FTIR) test was used to observe the chemical structure changes of the materials, and scanning electron microscopy (SEM) images were used to show the surface morphology changes of the materials. For electrochemical performance evaluation, VMP Bio-Logic tester was used to test the cyclic voltammetry (CV), Galvano static charge-discharge, electrical impedance spectroscopy (EIS), rate capability, and cycle life of materials. For mechanical behavior evaluation, dynamic mechanical analyses DMA (RSA 2) test in tension mode was performed to test the stress- strain curves and Young modulus (E) for all samples.

Chapter 4: *Results and Discussion*

We mentioned in chapter 3 about the preparation methods of PANI-PEO samples by using solution blending method or solution casting method. PANI monomers with phytic acid were blended with PEO solution, and then the polymerization process was done by using APS as an oxidative and an initiator to initiate the polymerization process.[8] PANI has three oxidation states (y) named as leucoemeraldine base y = 1 (fully reduced), pernigraniline y = 0 (fully oxidized), and emerladine base y = 0.5 (alternative reduced and oxidized units). The first two oxidative state are nonconductive forms. Emerladine base was doped and protonated by phytic acid to produce an electrically conductive emerladine salt which is the basic unit that used to prepare 3D nanostructure conductive polymer hydrogels (CPHs). Figure 12 shows the oxidation states of aniline monomers.[39]

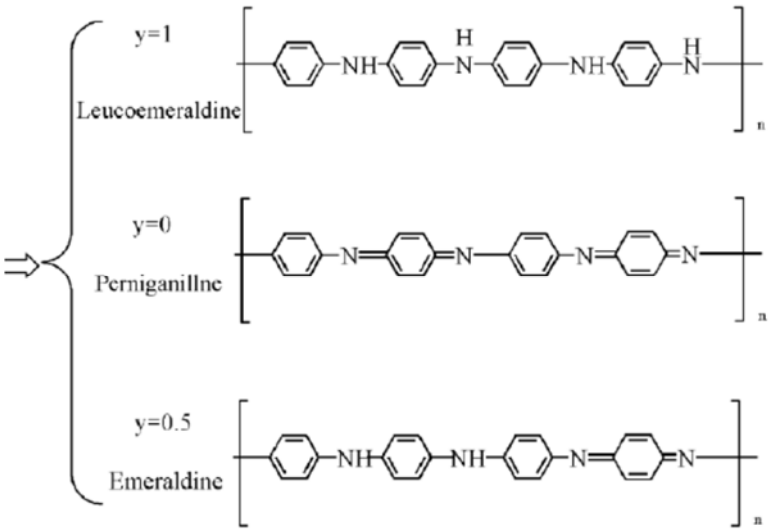

Figure 12. Basic oxidation states of aniline monomers.[39]

Polyaniline could interact with water soluble polymers such as PVA and PEO to produce a mixed phase thin film by two different mechanisms.[40, 41] The first one is the hydrogen bond interactions between undoped emerladine base form of polyaniline and water soluble polymers such as (PEO).[42, 43] PANI has amine and imine sites along the polymer backbone, and these sites work as hydrogen donors for oxygen functional groups of PEO that works as hydrogen acceptors to form strong bonding with PANI.[43] H-bonding mechanism may work with our doped (charged gel), so it depends on the degree of protonation of emerladine by phytic acid. For doped protonated polymer (our gel case), often the electrostatic interaction between oppositely charged polymers is the mechanism for producing homogenous thin film.[43] In order to analyze the mechanism of interaction between PANI/PEO, we tested the chemical structure of the hydrogel by Fourier transform infrared (FTIR) spectroscopy test.

4.1. Structure and Morphology Characterization for CPHs

Fourier transform infrared (FTIR) spectroscopy test has been done to test our hydrogels. we test three different samples based on the variation in PEO percentage such as PANI-0% PEO, PANI-4% PEO, and PANI-6% PEO. Figure 13 shows the FTIR pattern for the three samples.

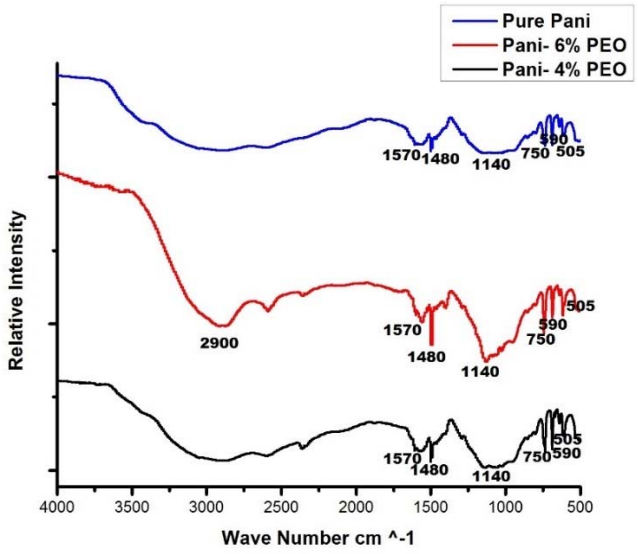

Figure 13. FTIR patterns for the synthesized hydrogel samples.

For all samples, characteristic peaks at 1570 cm^{-1} and 1480 cm^{-1} are the same, and they are corresponding to quinoid and benzenoid stretching vibration. These two peaks reflect that the material is emerladine salt based (aniline monomer doped by phytic acid).[8] peaks closed to 1140 cm^{-1} are corresponding to N=Q=N stretching (Q quinoid ring). 1140 cm^{-1} peak also indicates the electron delocation in our conductive hydrogel. The absorption near 750 and 505 cm^{-1} is corresponding to the C–H bending vibrations within the 1,4− aromatic ring. For PANI-0% PEO, the spectral region between 2000-3000 cm^{-1} is attributed to the conduction of the free electron in the doped polymer.[8] Small differences in the FTIR spectrum for the three samples are observed around 3500-2750 cm^{-1}. Usually H-bonding interaction occurred at 3300 cm^{-1} which is not available in our samples.[42]

Except the peak at 2900 cm^{-1} peak in PANI-6% PEO, the region between 3500-2250 cm^{-1} in PANI-0% PEO and other samples, has no clear differences that could be observed in the FTIR patterns which means that there is no H-bonding interaction between PANI and

PEO in the PANI-4% PEO and PANI-6% PEO samples.[42] This observation confirms that PANI/PEO were bonded via the electrostatic interaction mechanism (usually for protonated polymer gels). The specific peak at the spectral region around 2900 cm^{-1} for PANI-6% PEO is corresponding to The "C-H symmetric and asymmetric stretching vibrations of PEO".[42] Also, this peak can be observed on the FTIR pattern of PANI-4% PEO with less intensity than PANI-6% PEO. This is also related to the C-H bonds stretching of PEO.

X- ray diffraction test (XRD) has been done for Pure PEO and for our hydrogel samples. Figure 14. (A) shows the XRD patterns of pure PEO powder. (B) XRD patterns for our synthesized hydrogel samples.

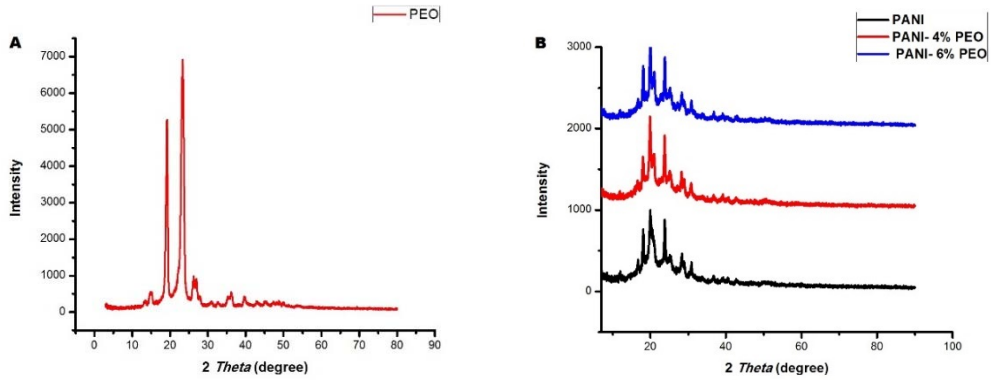

Figure 14. XRD patterns of PEO and hybrid gels. (A) Pure PEO polymer. (B) The synthesized hydrogel samples.

The pure PEO XRD pattern has to characteristics peaks at 2Θ = 20° and 23°. These two peaks are Bragg's peaks, and they reflect the crystalline nature of the PEO polymer.[44] PEO was widely used as a polymer matrix for polymer gel electrolytes because it is a water soluble polymer, and it could easily form a thick gel with water, but the main problem is

the crystalline nature of PEO which is clearly observed by Bragg's peaks. The crystalline nature of PEO is considered as the main obstacle for getting large ionic conductivity. Many materials have been added to PEO gel such as salts, bases, and acids. These materials could decrease the crystalline nature of PEO.

XRD pattern of our conductive hydrogels indicates that adding small percentages of PEO (4%, and 6%) to the pure PANI hydrogel doesn't change the crystallinity of the blend (PANI + PEO). This could be observed from figure 14 (B). There are five peaks between $2\Theta = 17°$ and $30°$. These peaks reflect the semi crystalline nature of our hydrogels.[45] We followed the same preparation method of the pure PANI gel in reference,[8] but the difference is we sonicate solution B for pure PANI gel and solution B + PEO of PANI-PEO gels for 20 minutes to confirm the complete solubility of all components especially for PEO. After that, the polymerization process was done directly by adding solution A. The sonication process for 20 minutes made noticeable changes in the crystalline nature of the elements, as a result it produced semi crystalline hydrogel with these peaks.[45]

The morphology of the hydrogels was observed by high resolution SEM images. Figure 15 shows the SEM images of PANI, PEO, PANI-4% PEO, and PANI-6% PEO. Figure 15 (A) shows the 3D interconnected nanofibers of PANI-0% PEO. The 3D network plays an important rule of providing short pathways for electron transports. In addition, the porous structure with the range of different pore sizes could provide a good interfacial contact with the electrolyte via increasing the electrolyte penetration depth through the pores. Figure 15 (B) shows the surface morphology of PEO. Figure 15 (C) for PANI-4%

PEO, shows that some of PANI interconnected nanofibers in some areas were coated by PEO. Some of the PEO has filled the pores of PANI as shown in Figure 15 (D). The effect of PEO on the electrical and the mechanical properties depends on the weight percentage of PEO and the distribution of PEO inside the hybrid gel. Since we used small percentages of PEO (4%, and 6%), the electrical performance has a relatively small degradation. On the other hand, the mechanical behavior has a noticeable enhancement.

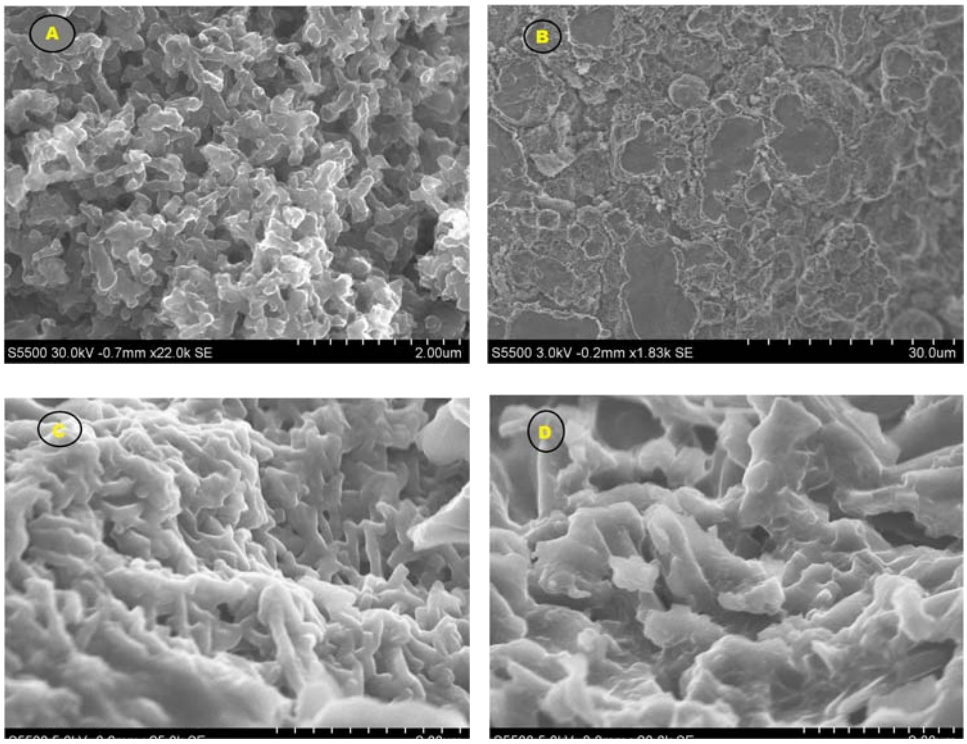

Figure 15. SEM images of the hydrogels. (A) Dendritic interconnected nanofiber of PANI-0% PEO. (B) The surface morphology of pure PEO. (C) SEM image of PANI-4% PEO shows that the dendritic interconnected nanofibers of PANI are coated with a layer of PEO. (D) SEM image of PANI-6% PEO shows that the PEO was deposited on the nanofibers and some of the PEO went through the porous structure of PANI.

4.2. Electrochemical Measurements

In order to test the electrochemical performance, VPM bio-logic system was used to characterize the half-cell performance (gel electrodes), and the same system was used to characterize the full cell electrochemical performance. Half-cell evaluation has been done by preparing our highly flexible gel electrodes (HFGEs). HFGEs was prepared by depositing the electroactive materials (PANI-0% PEO, PANI-4% PEO, and PANI-6% PEO) on a flexible carbon cloth substrate. HFGEs was the working electrode in the VPM system. We used 1 M H_2SO_4 liquid electrolyte to perform the test. For the half-cell evaluation test, we did the cyclic voltammetry (CV) test, Galvano static charge-discharge test, and the impedance spectroscopy test. Our full cell design (flexible symmetric gel supercapacitors) was designed by using two symmetric HFGEs, and PVA-1M H_2SO_4 was sandwiched between them. The electrochemical performance was characterized by cyclic voltammetry, Galvano static charge-discharge, impedance spectroscopy, rate capability, and cycling stability. In addition to the dynamic mechanical analysis (DMA), we did some electrochemical tests under different stress states such us CV and Impedance spectroscopy for bended, twisted, and wrapped full cell samples.

4.2.1. Half- Cell Electrochemical Measurements

2 mg mass load of (PANI-0%PEO, PANI-4%PEO, and PANI-6%PEO) were coated on (1 cm x 1 cm) flexible carbon cloth substrates. 1M H_2SO_4 liquid acidic electrolyte was used to characterize the gels. CV, and discharge curves are shown in Figure 16.

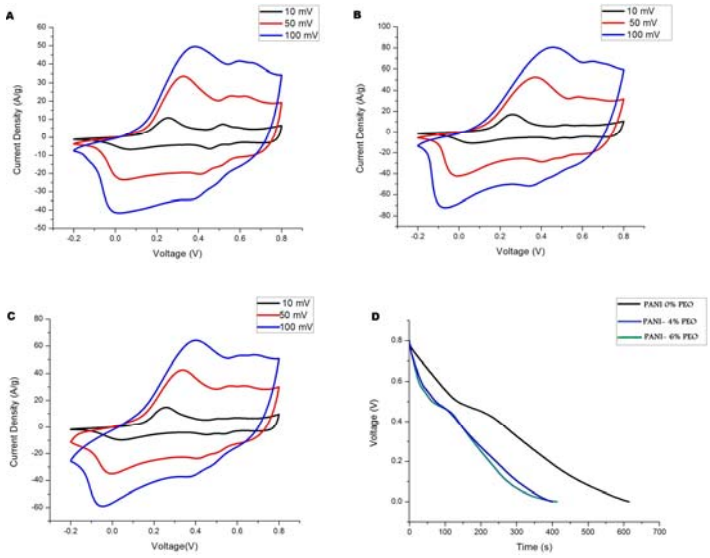

Figure 16. Cyclic voltammetry and discharge curves of hydrogels. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO. (D) Discharge curves at a current density of 0.5 A/g for the same hydrogels.

Cyclic voltammetry test of hydrogel samples (Figure 16 A, B, C) was done at different scan rates ranging as 10 mV/s, 50 mV/s, and 100 mV/s. The potential window is 1 Volt (- 0.2 to 0.8 V). All CV curves indicate a good electrochemical performance during the charge-discharge processes. The characteristics charge-discharge peaks on the CV curves represent the pseudo-capacitive reversible redox reactions (faradic reactions), which indicate that our hydrogels are pseudo- capacitive materials. Shifting in the CV discharge curves toward the lower voltage during the discharge indicates that the material has a good discharge capacitance at lower voltages. Specific capacitance of the hydrogel can be calculated either by integrating the area under the CV curve (equation 1),[46, 47] or by the

Galvano-static discharge curve (equation 2) shown in Figure (16 D).

$$c = \int_{E1}^{E2} \frac{i(E)dE}{2(E2-E1)mv} \quad \text{.....(1)}^{46,47}$$

$$c = \frac{i*\Delta t}{\Delta E*m} = \frac{Q}{\Delta E*m} \quad \text{.....(2)}^{47}$$

From equation (1), C is the specific capacitance. E1, E2 are the cutoff Voltages in CV curves, and *i(E)* is the instantaneous current. (E1 – E2) is the potential window, and the integration of i (E) dE is the total voltametric charge.[46] From equation 2, i is the applied current, and Δt is the discharge time. ΔE is the potential window (V), and m is the sample's mass load. Q is the stored charge which equal to i Δt.[47] To calculate the specific capacitance of the hydrogels, we used equation (2). The specific capacitance of PANI-0% PEO is 380 F/g. 266 F/g, and 250 F/g for PANI-4% PEO and PANI-6% PEO respectively. The specific capacitance was calculated based on 0.5 A/g current density, and the mass load is 2 mg. The specific capacitance has been decreased when the PEO was used, which is normal because PEO is a nonconductive hydrogel, and it was used to enhance the mechanical properties of hydrogels. Impedance spectroscopy test is an important factor in the electrochemical performance evaluation of our hydrogels. Figure 17 shows the impedance test of our hydrogels.

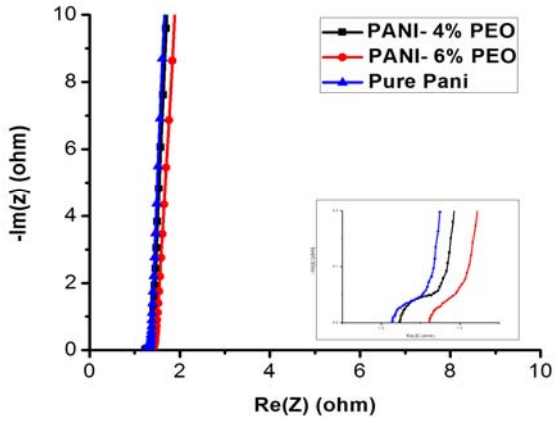

Figure 17. Impedance curves of hydrogel based electrodes.

The equivalent series resistance is calculated at a high frequency (100 kHz), and It found to be between (1.2–1.5 Ω), which is small values for 2 mg/cm^2 mass loads of our hydrogels. An ideal capacitive behavior could be observed at nearly vertical shape of curves at low frequency. In addition, the charge transfer resistance could be estimated from the semi circles, and it was estimated as less than 0.1 Ω. The smaller value of the charge transfer resistance reflects the most favorable ion transport in the porous nanostructured hydrogels.[8] Adding small percentages of PEO such as 4% and 6% cause a very small increasing in the resistance of the hydrogel, which is normal result in term of electrochemical performance evaluation.

4.2.2. Full cell Electrochemical Measurements

We designed three flexible gel supercapacitors based on the electroactive materials (hydrogels) that were deposited on the carbon cloth substrates. The first gel super capacitor was based on PANI-0% PEO, and the second was PANI-4% PEO. The third type was PANI-6% PEO. In next step, we will make a wide comparison between them in terms of electrochemical performance and mechanical behaviors. Figure 18 shows the cyclic voltammetry test for these samples.

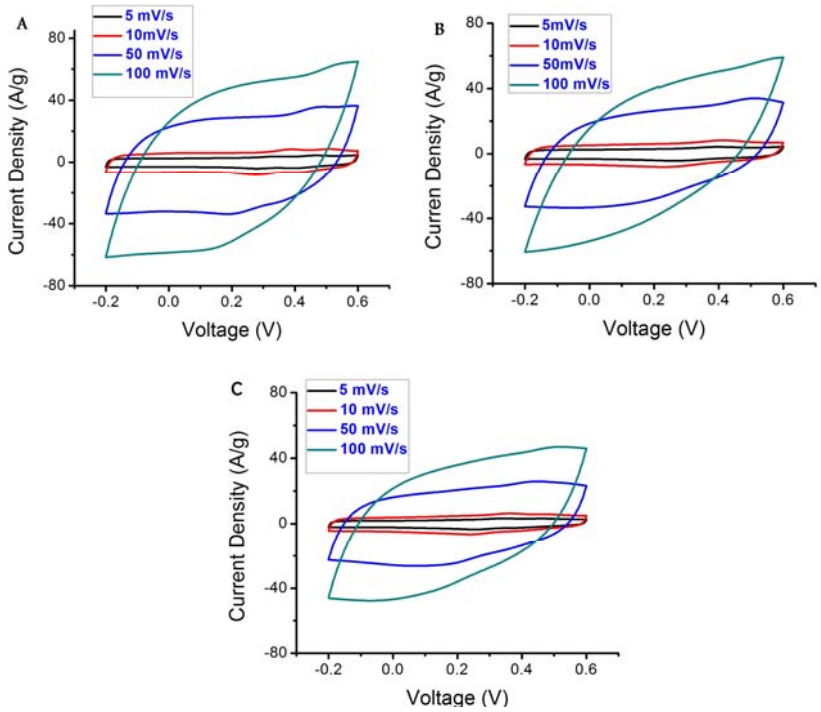

Figure 18. Cyclic voltammetry curves of gel supercapacitors. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO.

Cyclic voltammetry tests were done at different scan rates ranging as (5, 10, 50, 100) mv/S. The area under the curves indicates the specific capacitance of the full cell, and

it is clear that PANI-0% PEO (figure 18 A) has the largest area, which means that PANI-0% PEO has the largest specific capacitance followed by PANI-4% PEO and then PANI-6% PEO. As a comparison between the half- cell cyclic voltammetry and the full cell cyclic voltammetry, the full cell curves doesn't show big characteristic redox peaks like those that clearly seen in CV test of the half- cell (figure 16). The reason is in the half-cell evaluation, we used a liquid H_2SO_4 electrolyte, which will facilitate the ion transport between the two electrodes. As a result, the redox reversible reactions (faradic) will occur easily. In the full cell test, we used PVA-H_2SO_4 gel electrolyte sandwiched between two symmetric gel electrodes; therefore, ionic movement in the gel electrolyte will be much slower than their movement in liquid electrolyte. As a result, there is no enough time for redox reaction to be occurred widely, so we do not see clear peaks on the cyclic voltammetry test of the full cell for all samples.[38] Galvano-static charge-discharge test is also an important factor in the electrochemical performance evaluation of the full cells. It gives the more appropriate way to estimate the specific capacitance correctly. Equation 2 was used to calculate the specific capacitance for the three full cells. Before calculating the specific capacitance, we need to know material's behaviors under Galvano static charge-discharge test. Figure 19 shows the Galvano static charge discharge for three cells.

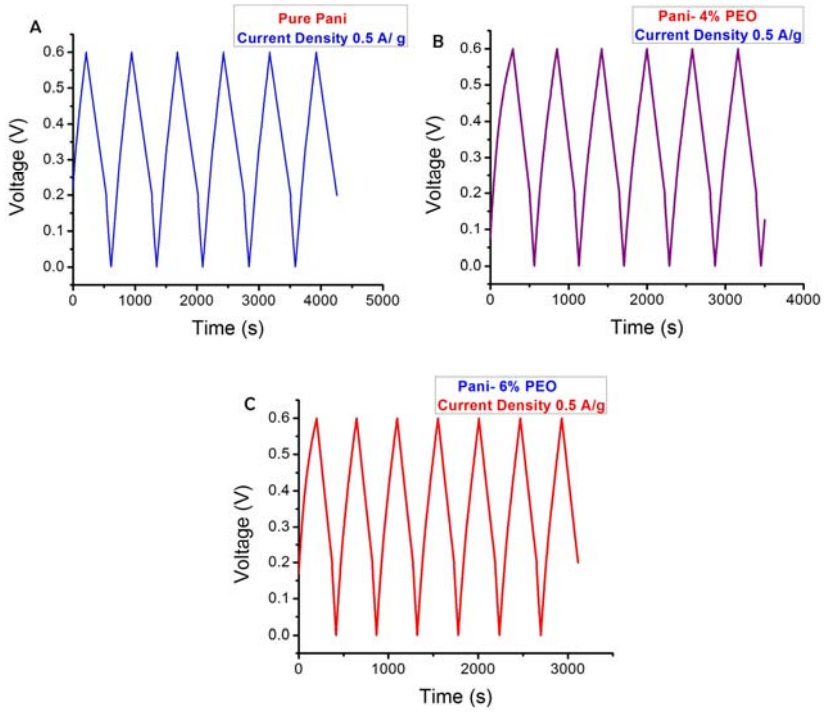

Figure 19. Galvano static charge-discharge test for gel supercapacitors. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO.

Galvano static charge-discharge test was done at 0.5 A/g current density for all gel supercapacitors, and it shows symmetric charge-discharge curves at the voltage range of (-0.2 to 0.6). The specific capacitance was calculated by using equation 2 multiplied by 2, because during the test, we counted one electrode's mass load (3 mg each electrode). The real specific capacitance for the full cells must be calculated depending on 2 symmetric electrode's mass loads (6 mg).[48] The specific capacitance of PANI-0% PEO (gel super capacitor) is 350 F/g. PANI-4% PEO has a specific capacitance of 275 F/g, and PANI-6% PEO has a specific capacitance of 213 F/g.

The gel supercapacitors have been exhibited good rate capabilities at different current densities ranging as (0.5, 0.7, 0.8, 0.9, 1) A/g. Gel supercapacitor performance at these ranges was good, and there was a small fad in the specific capacitance when the higher current densities were used. The specific capacitance fad will be higher at higher current densities (2 A/g and over) due to the slower ionic transport speed in the gel electrolyte. Figure 20 shows the rate capabilities of PANI-0% PEO, PANI-4% PEO, and PANI-6% PEO.

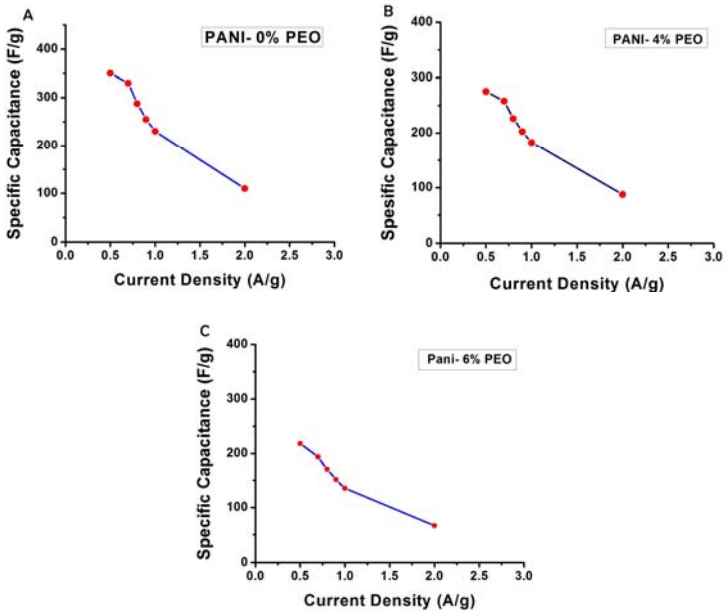

Figure 20. Rate capability test for gel supercapacitors. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO. The rate capability test has been done at different current densities ranging as (0.5, 0.7, 0.8, 0.9, 1, 2) A/g.

Cycling performance (cycling stability) is also an important factor which shows the gel supercapacitor electrochemical performance for a long term of working. It also

indicates that the percentage of the specific capacitance retention after a specific life time. Figure 21 shows 500 cycles cycling performance of PANI-0% PEO, PANI-4% PEO, and PANI-6% PEO gel supercapacitors at a current density of 0.5 A/g.

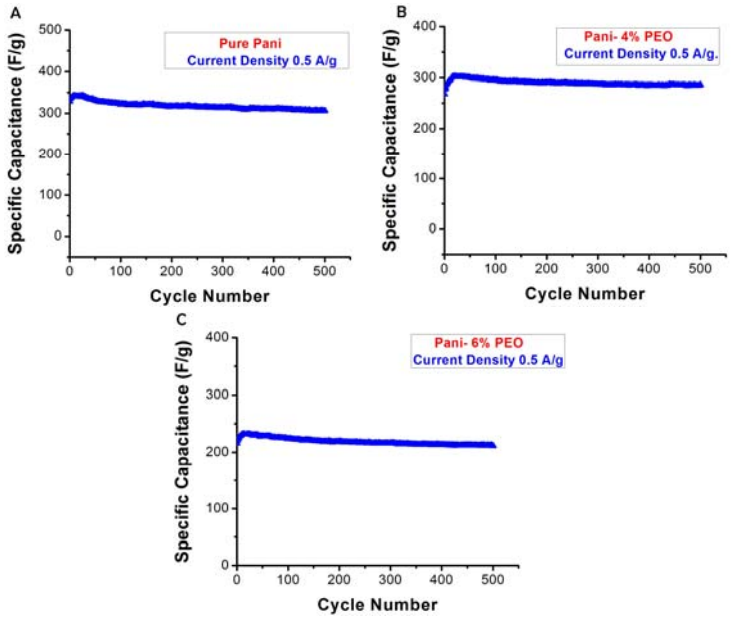

Figure 21. The cycling performance of gel supercapacitors. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO.

From Figure 21, it is clear that after 25 cycles (in all samples) the specific capacitance has been increased and it has become stable with a very small degradation along the curves to the end. Reasons are that some electrochemical activation has been occurred to the material during the charge-discharge processes after some cycles,[49] and another reason may be the increase in the electrode-electrolyte interfacial contact via increasing the wettability of electrodes by electrolyte during the time. The capacity retention between 25-500 cycles for PANI-0% PEO was 92%. The capacity retention for PANI-4% PEO was 95%, and the capacity retention of PANI-6% PEO was 95%. The small

differences in the specific capacitance retention percentages of the three gel supercapacitors is due to the contribution of PEO, which may help to release the PANI chains strain due to the volume change during the charge-discharge processes.[49, 50] An another reason is the availability of PEO in the gel electrodes could increase the interfacial contact with the gel electrolyte. To confirm the idea of the flexibility increasing with increasing the PEO percentage in the hybrid gel, we did two electrochemical tests under different bending stresses. The first test was the impedance test under flat condition, and under the bending the samples around 3 mm radius bar. Figure 22 shows the impedance spectroscopy test under flat and bending conditions for three gel supercapacitors.

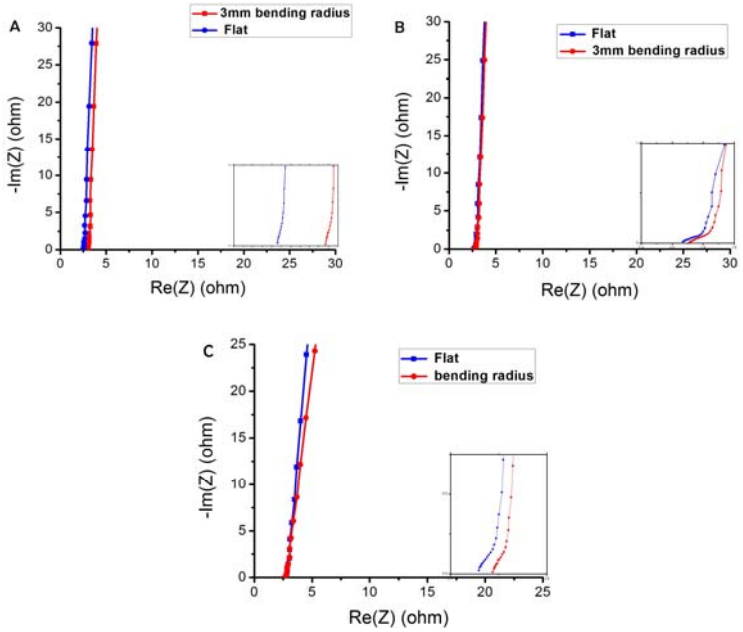

Figure 22. Impedance test under flat and bending conditions for gel supercapacitors. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO. for bending, the materials were bended around 3mm radius bar.

Both of the three supercapacitors exhibited good equivalent series resistances (ESRs) ranging between (2.5-3 Ω). For PANI-0% PEO (figure 22 A), the resistance under bending is higher than the resistance without bending by the order of 0.5 Ω, while other samples (Figure 22 B, C) have less than 0.1 Ω difference. The reason is that in the sample (A), there may be some small micro-cracks in the gel structure under the critical bending stress, which lead to increase the difference in the resistance of PANI-0% PEO in the flat and in the bending cases. In the PANI-4% and PANI-6% PEO, there was a very small deference (>0.1 Ω) in the values of the resistance under different stress states. The reason is the availability of PEO in the hybrid gel, which helps to release and dissipate the mechanical stress that applied to the hydrogel in bending situation. Over all, the values of the resistance obtained from figure 22 are higher than the values of the resistance obtained from figure 17 (half-cell impedance) because we used liquid electrolyte in half- cell characterization and we used PVA-H_2SO_4 gel electrolyte for the full cell design.

Cyclic voltammetry (CV) test at different bending stress states was used as a second test to confirm that adding PEO as a plasticizer polymer will lead to increase the flexibility of the hybrid gel electrodes. CV at 50 mV/s scan rate has been done at: flat condition, bending around 3mm, and 8mm radius rounded bars, and wrapping around 3mm radius bar.

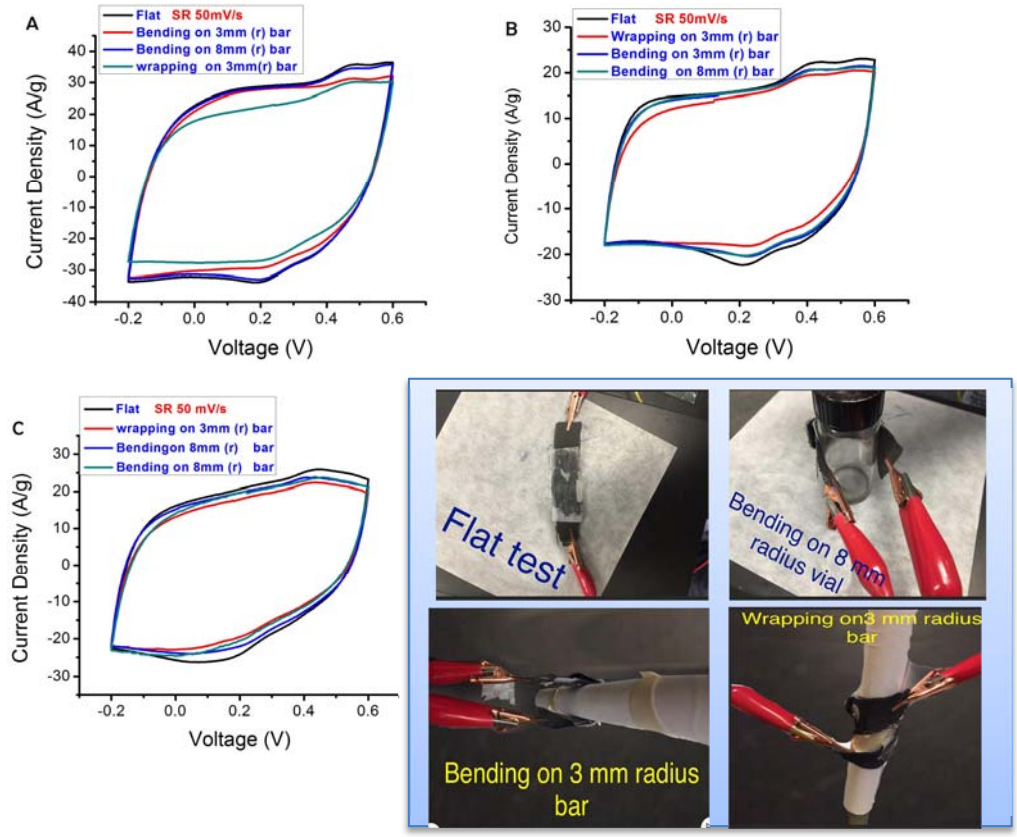

Figure 23. Cyclic voltammetry test under different stress states. (A) PANI-0% PEO. (B) PANI-4% PEO. (C) PANI-6% PEO. The inset photos show the gel supercapacitors under different stress states.

All samples have been exhibited good flexibility under different stress states. Wrapping the gel supercapacitors around 3 mm radius was a critical test for the samples, because the whole material will be subjected to the bending stress. PANI-0% PEO has a noticeable decreasing in the CV curve under wrapping condition, while other samples didn't show like this behavior. This case confirms that the PANI-0% PEO has less flexibility than others. Energy density and power density are important parameters in the

performance evaluation for all samples. Equation 3 and equation 4 can be used to calculate the energy density and the power density of the full cells [50].

$$E = \frac{0.5*C*V\hat{}2}{m} \quad \text{..... (3)}^{51}$$

$$P = \frac{V\hat{}2}{4Rm} \quad \text{..... (4)}^{51}$$

C is the capacitance of the full cell. V is the applied potential window. R is the equivalent series resistance, and m is the total mass load of the electroactive material (hydrogel). The energy density of PANI-0% PEO gel super capacitor is 112 Wh/kg, and the specific power is 21.3 kW/kg. the energy density and the power density of PANI-4% PEO are 88 Wh/kg, and 19 kW/kg respectively. The energy density and the power density of PANI-6% PEO are 68.16 Wh/kg, and 18.3 kW/kg respectively. The energy density and the power density values of the gel supercapacitors indicate that they could be used to power relatively high power flexible electronics such as role up screens and bendable electronics. As reported in other papers, rechargeable batteries have high energy densities but low power densities, while electric double layer capacitors exhibited lower energy density and higher power density. The flexible supercapacitors (pseudo-capacitive) have high power densities and good energy densities, so the flexible supercapacitors reduce the energy density gap between rechargeable batteries and electric double layer capacitors.

4.3. Dynamic Mechanical Analysis (DMA) Test

DMA test has been done for the gel electrodes to test the flexibility and the ductility of our devices. DMA has been done by using RSA G2 tester under tension mode. Our hydrogels were deposited on the carbon cloth substrate (electrodes) with specific dimensions, and the electrodes were subjected to a uniaxial force (tension) for a period of time under 25°C ambient temperature. The electrode has a length of 20.50 mm, and it has a width of 10 mm with the thickness of 0.41 mm. The calculated young's modules were 55 MPa for PANI-0% PEO, 45 MPa for PANI-4% PEO, and 29.2 MPa for PANI-6% PEO. Test results were calculated from figure 24 below. Young modulus values confirm that the PANI-6% PEO is more flexible and more ductile than other samples, which proves our idea of increasing the flexibility when PEO has been added to the gel.

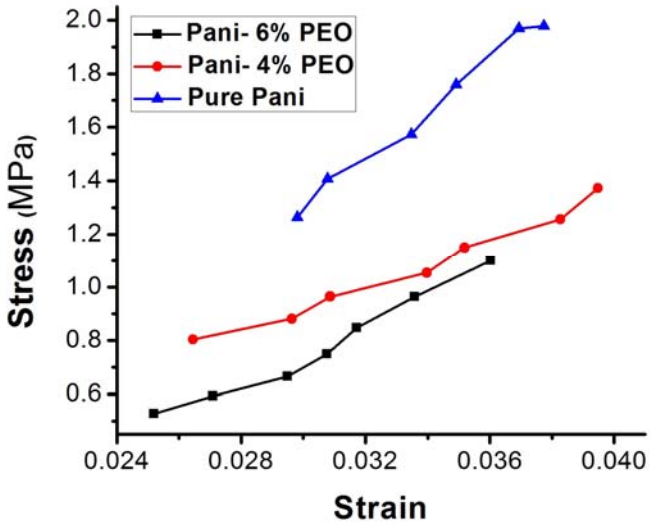

Figure 24. Dynamic mechanical test of the flexible gel electrodes.

Chapter 5: *Conclusion*

In this thesis, we proposed a new idea of synthesizing three types of bendable, twistable, and foldable gel supercapacitors based on the conductive hydrogel (3D nanostructured PANI) and the nonconductive gel (PEO). We classified our gel supercapacitors based on the PEO percentage in the hybrid gel electrodes. PEO availability in the gel electrodes serves to increase the flexibility and the ductility of the devices, and at the same time provides a good interfacial contact between the gel electrodes and the gel electrolyte, which will lead to increase the ionic conductivity. The 3D hierarchically nanostructured conductive polymer hydrogel (PANI) contributed to provide high electrochemical properties such as high specific capacitance, high energy density, and high power density to the gel supercapacitors. The 3D interconnected nanofibers network with porous structure of PANI hydrogel provide short ways for electrons to transport easily. In addition, the porous structure provides easy way for ions to go through these pores which provides a good ionic penetration depth, as a result it leads to increase the electrode-electrolyte contact. The first gel supercapacitor was based on PANI-0% PEO gel electrodes, which exhibited high electrochemical properties and lower mechanical flexibility than other two types. The second type was based on PANI-4% PEO gel electrodes, which exhibited intermediate electrochemical and mechanical properties compared with other gel supercapacitors. The third type was based on PANI-6% PEO gel electrodes, which exhibited lower electrochemical performance and higher mechanical properties than other samples. Producing these types of gel supercapacitors was very beneficial, and in general, designing flexible gel supercapacitors by blending conductive

and nonconductive hydrogels together to design flexible gel electrodes was beneficial through: cost reduction, carbon nanomaterials free, better safety because PEO is nontoxic material, and time reduction. The synthesized gel electrodes may be not only used for the flexible gel supercapacitors, but also they could be used in the synthesizing process of flexible gel rechargeable batteries.

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